



\$ 442 / 101

07/436464

A

- 1 -

CH-1763

521
Fire Extinguishing Composition and Process

Field of Invention

5 This invention relates to compositions for use in preventing and extinguishing fires based on the combustion of combustible materials. More particularly, it relates to such compositions that are highly effective and "environmentally safe".
10 Specifically, the compositions of this invention have little or no effect on the ozone layer depletion process; and make no or very little contribution to the global warming process known as the "greenhouse effect". Although these compositions have minimal
15 effect in these areas, they are extremely effective in preventing and extinguishing fires, particularly fires in enclosed spaces.

CLU/C
p
Background of the Invention and Prior Art

20 In preventing or extinguishing fires, two important elements must be considered for success: (1) separating the combustibles from air; and (2) avoiding or reducing the temperature necessary for combustion to proceed. Thus, one can smother small fires with
25 blankets or with foams to cover the burning surfaces to isolate the combustibles from the oxygen in the air. In the customary process of pouring water on the burning surfaces to put out the fire, the main element is reducing temperature to a point where combustion
30 cannot proceed. Obviously, some smothering or separation of combustibles from air also occurs in the water situation.

The particular process used to extinguish fires depends upon several items, e.g. the location of
35 the fire, the combustibles involved, the size of the

- 1 -

2

fire, etc. In fixed enclosures such as computer rooms, storage vaults, rare book library rooms, petroleum pipeline pumping stations and the like, halogenated hydrocarbon fire extinguishing agents are currently preferred. These halogenated hydrocarbon fire extinguishing agents are not only effective for such fires, but also cause little, if any, damage to the room or its contents. This contrasts to the well-known "water damage" that can sometimes exceed the fire damage when the customary water pouring process is used.

3
√ # #
The halogenated hydrocarbon fire extinguishing agents that are currently most popular are the bromine-containing halocarbons, e.g. bromotrifluoromethane (CF_3Br , Halon 1301) and bromochlorodifluoromethane (CF_2ClBr , Halon 1211). It is believed that these bromine-containing fire extinguishing agents are highly effective in extinguishing fires in progress because, at the elevated temperatures involved in the combustion, these compounds decompose to form products containing bromine atoms which effectively interfere with the self-sustaining free radical combustion process and, thereby, extinguish the fire. These bromine-containing halocarbons may be dispensed from portable equipment or from an automatic room flooding system activated by a fire detector.

In many situations, enclosed spaces are involved. Thus, fires may occur in rooms, vaults, enclosed machines, ovens, containers, storage tanks, bins and like areas. The use of an effective amount of fire extinguishing agent in an enclosed space involves two situations. In one situation, the fire extinguishing agent is introduced into the enclosed space to extinguish an existing fire; the second

situation is to provide an ever-present atmosphere containing the fire "extinguishing" or, more accurately the fire prevention agent in such an amount that fire cannot be initiated nor sustained. Thus, in U.S.

5 Patent 3,844,354, Larsen suggests the use of
chloropentafluoroethane ($\text{CF}_3\text{-CF}_2\text{Cl}$) in a total flooding
system (TFS) to extinguish fires in a fixed enclosure,
the chloropentafluoroethane being introduced into the
fixed enclosure to maintain its concentration at less
10 than 15%. On the other hand, in U.S. Patent 3,715,438,
Huggett discloses creating an atmosphere in a fixed
enclosure which does not sustain combustion. Huggett
provides an atmosphere consisting essentially of air, a
perfluorocarbon selected from carbon tetrafluoride,
15 hexafluoroethane, octafluoropropane and mixtures
thereof.

It has also been known that bromine-
containing halocarbons such as Halon 1211 can be used
to provide an atmosphere that will not support
20 combustion. However, the high cost due to bromine
content and the toxicity to humans i.e. cardiac
sensitization at relatively low levels (e.g. Halon 1211
cannot be used above 1-2 %) make the bromine-containing
materials unattractive for long term use.

14
25 In recent years, even more serious objections
to the use of brominated halocarbon fire extinguishants
has arisen. The depletion of the stratospheric ozone
layer, and particularly the role of chlorofluorocarbons
(CFC's) have led to great interest in developing
30 alternative refrigerants, solvents, blowing agents,
etc. It is now believed that bromine-containing
halocarbons such as Halon 1301 and Halon 1211 are at
least as active as chlorofluorocarbons in the ozone
layer depletion process.

35 While perfluorocarbons such as those
suggested by Huggett, cited above, are believed not to

3
have as much effect upon the ozone depletion process as chlorofluorocarbons, their extraordinarily high stability makes them suspect in another environmental area, that of "greenhouse effect". This effect is
5 caused by accumulation of gases that provide a shield against heat transfer and results in the undesirable warming of the earth's surface.

There is, therefore, a need for an effective fire extinguishing composition and process which
10 contributes little or nothing to the stratospheric ozone depletion process or to the "greenhouse effect".

It is an object of the present invention to provide such a fire extinguishing composition; and to provide a process for preventing and controlling fire
15 in a fixed enclosure by introducing into said fixed enclosure, an effective amount of the composition.

CLV/c
p
#13
✓ #13
✓ #13
✓ #13
Summary of Invention

The present invention is based on the finding
20 that an effective amount of a composition consisting essentially of at least one partially fluoro-substituted propane selected from the group of the heptafluoropropanes ($\text{CF}_3\text{-CF}_2\text{-CHF}_2$ and $\text{CF}_3\text{-CFH-CF}_3$), also known as HFC-227ca and HFC-227ea, the
25 hexafluoropropanes ($\text{CF}_3\text{-CH}_2\text{-CF}_3$, $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{F}$ and $\text{CF}_2\text{H-CF}_2\text{-CF}_2\text{H}$), also known as HFC-236fa, HFC-236cb and HFC-236ca, and the chlorohexafluoropropanes ($\text{CFClF-CF}_2\text{-CF}_3$, $\text{CHF}_2\text{-CF}_2\text{-CF}_2\text{Cl}$, $\text{CF}_3\text{-CHCl-CF}_3$, $\text{CF}_3\text{-CHF-CF}_2\text{Cl}$, and $\text{CHF}_2\text{-CFCl-CF}_3$), also known as
30 HCFC-226ca, HCFC-226cb, HCFC-226da, HCFC-226ea and HCFC-226ba, will prevent and/or extinguish fire based on the combustion of combustible materials, particularly in an enclosed space, without adversely affecting the atmosphere from the standpoint of ozone
35 depletion or "greenhouse effect". Also useful in this invention are those partially fluoro-substituted.

propanes with normal boiling points above 25°C, i.e. HFC-236ea, HCFC-225ca, HCFC-225cb, HCFC-225aa, HCFC-225da, HCFC-235ca, HCFC-235cb, HCFC-235cc, and HCFC-235fa.

5 The partially fluoro-substituted propanes
above may be used in conjunction with as little as 1%
of at least one halogenated hydrocarbon selected from
the group of difluoromethane (HFC-32),
chlorodifluoromethane (HCFC-22), 2,2-dichloro-
10 1,1,1-trifluoroethane (HCFC-123),
1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a),
2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124),
1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a),
pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane
15 (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a),
3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca),
1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb),
2,2-dichloro-1,1,1,3,3-pentafluoropropane (HCFC-225aa),
2,3-dichloro-1,1,1,3,3-pentafluoropropane (HCFC-225da),
20 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca),
1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea),
1,1,1,2,3,3,3-hexafluoropropane (HFC-236ea),
1,1,1,3,3,3,3-hexafluoropropane (HFC-236fa),
1,1,1,2,2,3,3-hexafluoropropane (HFC-236cb),
25 1,1,2,2,3,3,3-hexafluoropropane (HFC-236ca),
3-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235ca),
3-chloro-1,1,1,2,2-pentafluoropropane (HCFC-235cb),
1-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235cc),
3-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235fa),
30 3-chloro-1,1,1,2,2,3-hexafluoropropane (HCFC-226ca),
1-chloro-1,1,2,2,3,3-hexafluoropropane (HCFC-226cb),
2-chloro-1,1,1,3,3,3-hexafluoropropane (HCFC-226da),
3-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ea),
and 2-chloro-1,1,1,2,3,3-hexafluoropropane
35 (HCFC-226ba).

CLU/c
p

Preferred Embodiments

The partially fluoro-substituted propanes, when added in adequate amounts to the air in a confined space, eliminate the combustion-sustaining properties of the air and suppress the combustion of flammable materials, such as paper, cloth, wood, flammable liquids, and plastic items, which may be present in the enclosed compartment.

These fluoropropanes are extremely stable and chemically inert. They do not decompose at temperatures as high as 350°C to produce corrosive or toxic products and cannot be ignited even in pure oxygen so that they continue to be effective as a flame suppressant at the ignition temperatures of the combustible items present in the compartment.

The preferred fluoropropanes are HFC-227ca, HFC-227ea, HFC-236cb, HFC-236fa, HFC-236ca and HFC-236ca, i.e. the HFC-227 and 236 series. The particularly preferred fluoropropanes HFC-227ca, HFC-227ea, HFC-236cb and HFC-236fa are additionally advantageous because of their low boiling points, i.e. boiling points at normal atmospheric pressure of less than 1.2°C. Thus, at any low environmental temperature likely to be encountered, these gases will not liquefy and will not, thereby, diminish the fire preventive properties of the modified air. In fact, any material having such a low boiling point would be suitable as a refrigerant.

The heptafluoropropanes HFC-227ea and HFC-227ca are also characterized by an extremely low boiling point and high vapor pressure, i.e. above 44.3 and 42.0 psig at 21°C respectively. This permits HFC-227ea and HFC-227ca to act as their own propellants in "hand-held" fire extinguishers. Heptafluoropropanes (HFC-227ea and HFC-227ca) may also be used with other

materials such as those disclosed on page 5 of this specification to act as the propellant and co-extinguishant for these materials of lower vapor pressure. Alternatively, these other materials of lower vapor pressure may be propelled from a portable fire extinguisher or fixed system by the usual propellants, i.e. nitrogen or carbon dioxide. Their relatively low toxicity and their short atmospheric lifetime (with little effect on the global warming potential) compared to the perfluoroalkanes (with lifetimes of over 500 years) make these fluoropropanes ideal for this fire-extinguisher use.

To eliminate the combustion-sustaining properties of the air in the confined space situation, the gas or gases should be added in an amount which will impart to the modified air a heat capacity per mole of total oxygen present sufficient to suppress or prevent combustion of the flammable, non-self-sustaining materials present in the enclosed environment.

The minimum heat capacity required to suppress combustion varies with the combustibility of the particular flammable materials present in the confined space. It is well known that the combustibility of materials, namely their capability for igniting and maintaining sustained combustion under a given set of environmental conditions, varies according to chemical composition and certain physical properties, such as surface area relative to volume, heat capacity, porosity, and the like. Thus, thin, porous paper such as tissue paper is considerably more combustibile than a block of wood.

In general, a heat capacity of about 40 cal./°C and constant pressure per mole of oxygen is more than adequate to prevent or suppress the combustion of materials of relatively moderate

S.D.A.

combustibility, such as wood and plastics. More
combustible materials, such as paper, cloth, and some
volatile flammable liquids, generally require that the
fluoro~~ethane~~^{PROPANE} be added in an amount sufficient to impart
5 a higher heat capacity. It is also desirable to
provide an extra margin of safety by imparting a heat
capacity in excess of minimum requirements for the
particular flammable materials. A minimum heat
capacity of 45 cal./°C per mole of oxygen
10 is generally adequate for moderately combustible
materials and a minimum of about 50 cal./°C per mole of
oxygen for highly flammable materials. More can be
added if desired but, in general, an amount imparting a
heat capacity higher than about 55 cal./°C per mole of
15 total oxygen adds substantially to the cost without any
substantial further increase in the fire safety factor.

Heat capacity per mole of total oxygen can be
determined by the formula:

T, 90X
PS
PHH

$$C_p^* = (C_p)_{O_2} + \frac{P_z}{P_{O_2}} (C_p)_z$$

wherein:

C_p^* = total heat capacity per mole of oxygen at
constant pressure;

PHH

25 P_{O_2} = partial pressure of oxygen;

PHH

P_z = partial pressure of other gas;

PHH

30 $(C_p)_z$ = heat capacity of other gas at constant
pressure.

P

The boiling points of the fluoropropanes used
in this invention and the mole percents required to
35 impart to air heat capacities (C_p) of 40 and 50 cal./°C
at a temperature of 25°C and constant pressure while

maintaining a 20% and 16 % oxygen content are tabulated below:

T_{100X^5}

	FC	Boiling point, °C.	20 % O ₂		16 % O ₂
			Cp=40 vol percent	Cp=50 vol percent	Cp=50 vol percent
10	236ea	26.2	4.5	13.5	4.5
	236fa	-0.7	4.5	13.0	4.5
	236cb	1.2	4.5	13.0	4.5
	236ca	10.0	4.5	13.5	4.5
	227ea	-18.0	4.0	12.0	4.0
	227ca	-17.0	4.0	12.0	4.0
15	225ca	53.0	3.8	11.0	3.8
	225cb	52.0	3.8	11.0	3.8
	225aa	55.4	3.8	11.0	3.8
	225da	50.4	3.5	10.8	3.5
	235ca	44.8	4.5	13.0	4.5
20	235cb	27.2	4.3	12.5	4.3
	235cc	36.1	4.3	12.5	4.3
	235fa	28.4	4.0	12.5	4.0
	226ca	20.0	4.0	11.5	4.0
	226cb	21.5	4.0	11.5	4.0
25	226da	14.5	4.0	11.0	4.0
	226ea	16.0	4.0	11.5	4.0
	226ba	16.4	4.0	11.5	4.0

p

Introduction of the appropriate fluoropropanes is easily accomplished by metering appropriate quantities of the gas or gases into the enclosed air-containing compartment.

The air in the compartment can be treated at any time that it appears desirable. The modified air can be used continuously if a threat of fire is constantly present or if the particular environment is

such that the fire hazard must be kept at an absolute minimum; or the modified air can be used as an emergency measure if a threat of fire develops.

DEP
The invention will be more clearly understood by referring to the examples which follow. The unexpected effects of the fluoropropanes, alone and in any of the aforementioned blends, in suppressing and combatting fire, as well as its compatability with the ozone layer and its relatively low "greenhouse effect", when compared to other fire-combatting gases, particularly the perfluoroalkanes and Halon 1211, are shown in the examples.

CLU/C²CL
AA
P
14
Example 1 - Fire Extinguishing Concentrations
AA

15 The fire extinguishing concentration of the fluoropropane compositions compared to several controls, was determined by the ICI Cup Burner method. This method is described in "Measurement of
20 Flame-Extinguishing Concentrations" R. Hirst and K. Booth, Fire Technology, vol. 13(4): 296-315 (1977).

Specifically, an air stream is passed at 40 liters/minute through an outer chimney (8.5 cm. I. D. by 53 cm. tall) from a glass bead distributor at its
25 base. A fuel cup burner (3.1 cm. O.D. and 2.15 cm. I.D.) is positioned within the chimney at 30.5 cm. below the top edge of the chimney. The fire extinguishing agent is added to the air stream prior to its entry into the glass bead distributor while the air
30 flow rate is maintained at 40 liters/minute for all tests. The air and agent flow rates are measured using calibrated rotameters.

Each test is conducted by adjusting the fuel level in the reservoir to bring the liquid fuel level
35 in the cup burner just even with the ground glass lip on the burner cup. With the air flow rate maintained

at 40 liters/minute, the fuel in the cup burner is ignited. The fire extinguishing agent is added in measured increments until the flame is extinguished. The fire extinguishing concentration is determined from the following equation:

$$\text{Extinguishing concentration} = \frac{F_1}{F_1 + F_2} \times 100$$

where F_1 = Agent flow rate
 F_2 = Air flow rate

Two different fuels are used, heptane and methanol; and the average of several values of agent flow rate at extinguishment is used for the following table.

Table 1
Extinguishing Concentrations of Certain Fluoropropane Compositions Compared to Other Agents

	Agent	Fuel		Flow Rate		
		Heptane	Methanol	Extinguishing Conc. (vol. %)	Air (l/min)	Agent (l/min)
	Fe#					Hept. Meth.
25	HFC-227ea	7.3	10.1	40.1	3.14	4.52
	HFC-236ea	10.2	8.4	40.1	4.55	3.68
	HCFC-235cb	6.2	8.2	40.1	2.60	3.57
	CF ₄	20.5	23.5	40.1	10.31	12.34
	C ₂ F ₆	8.7	11.5	40.1	3.81	5.22
30	H-1301*	4.2	8.6	40.1	1.77	3.77
	H-1211**	6.2	8.5	40.1	2.64	3.72
	CHF ₂ Cl	13.6	22.5	40.1	6.31	11.64

* CF₃Br

35 ** CF₂ClBr

Example 2

14

5 The ozone depletion potential (ODP) of the fluoropropanes and various blends thereof, compared to various controls, was calculated using the method described in "The Relative Efficiency of a Number of Halocarbon for Destroying Stratospheric Ozone" D. J. Wuebles, Lawrence Livermore Laboratory report UCID-18924, (January 1981) and "Chlorocarbon Emission Scenarios: Potential Impact on Stratospheric Ozone" D. J. Wuebles, Journal Geophysics Research, 88, 1433-1443 (1983).

15 Basically, the ODP is the ratio of the calculated ozone depletion in the stratosphere resulting from the emission of a particular agent compared to the ODP resulting from the same rate of emission of FC-11 (CFCl_3) which is set at 1.0. Ozone depletion is believed to be due to the migration of compounds containing chlorine or bromine through the troposphere into the stratosphere where these compounds are photolyzed by UV radiation into chlorine or bromine atoms. These atoms will destroy the ozone (O_3) molecules in a cyclical reaction where molecular oxygen (O_2) and $[\text{ClO}]$ or $[\text{BrO}]$ radicals are formed, those radicals reacting with oxygen atoms formed by UV radiation of O_2 to reform chlorine or bromine atoms and oxygen molecules, and the reformed chlorine or bromine atoms then destroying additional ozone, etc., until the radicals are finally scavenged from the stratosphere. It is estimated that one chlorine atom will destroy 10,000 ozone molecules and one bromine atom will destroy 100,000 ozone molecules.

20
25
30
35 The ozone depletion potential is also discussed in "Ultraviolet Absorption Cross-Sections of Several Brominated Methanes and Ethanes" L. T. Molina, M. J. Molina and F. S. Rowland" J. Phys. Chem. 86,

14F

2672-2676 (1982); in Bivens et al. U.S. Patent 4,810,403; and in "Scientific Assessment of Stratospheric Ozone: 1989" U.N. Environment Programme (21 August 1989).

5 In the following table, the ozone depletion potentials are presented for the fluoropropanes and the controls.

Table 2

	<u>Agent</u>	<u>Ozone Depletion Potential</u>
	HFC-236ea	0
	HFC-236fa	0
15	HFC-236cb	0
	HFC-236ca	0
	HFC-227ea	0
	HFC-227ca	0
	CF ₄	0
20	C ₂ F ₆	0
	H-1301	10
	CHF ₂ Cl	0.05
	H-1211	3
	CFCl ₃	1
25	CF ₃ -CF ₂ Cl	0.4

← 30

cm I claim:

35